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A temperature-controlled device for volumetric measurements of Helium adsorption in porous media.

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We describe a set-up for studying adsorption of helium in silica aerogels, where the adsorbed amount is easily and precisely controlled by varying the temperature of a gas reservoir between 80 K and 180 K. We present validation experiments and a first application to aerogels. This device is well adapted to study hysteresis, relaxation, and metastable states in the adsorption and desorption of fluids in porous media.

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1. INTRODUCTION

The technique of adsorption isotherms, which measures the adsorbed amount of a fluid in a porous medium as a function of the applied pressure, is a central tool in surface physics. On the applied side, isotherms are used to characterize the porous medium itself (distribution of pores sizes), while, on the fundamental side, they detect the phase transitions of the confined fluid¹. Adsorption of helium has been studied in a variety of materials with different topologies, such as grafoil, carbon nanotubes, or silica glasses. The case of silica aerogels has attracted attention in the recent years, since the early work of Wong and Chan². As in other porous media, experiments show that the isotherms are hysteretic between adsorption and desorption, and that condensation occurs over a range of pressures³⁻⁶. However, this range is unexpectedly narrow, compared to what could be expected from the wide distribution of "pores" sizes in aerogels, especially at low porosity^{3,7} or low temperature^{6,7}. Both facts are in agreement with recent theoretical work^{8,9}, according to which the shape of the isotherm, and its hysteresis, result from the disordered nature of the aerogel, rather than of its geometry or topology.

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In particular, the observed change of shape with porosity or temperature could sign the occurrence of a disorder induced, out-of-equilibrium, phase transition⁸. While this vision is supported by optical experiments¹¹, a challenge would be to study in detail the critical shape of the isotherm close to the transition. An other open problem in the context of adsorption is whether this hysteresis disappears at, or below, the bulk critical point.

Studying these questions require high resolution measurements of the isotherms. Usually, the adsorption curves are determined by a volumetric technique, by adding known doses of helium in successive steps and measuring the resulting equilibrium pressure after each step. This has several drawbacks. If large steps are used, the flow rate at which helium is injected is initially large, and this warms up the sample, due to the heat released by the adsorption process. This might perturb the process in an irreversible way, when the system is unable to reach true thermal equilibrium, as is the case in aerogels. On the other hand, if small steps are used, measurements errors accumulate, resulting in a large error on the adsorbed amount. In our previous work, we instead used a continuous method, in which helium is injected at a regulated flowrate, small enough (typically 0.1 STP cc/min) to minimize the thermal perturbation. Due to this small value (2% of the range of our regulated flowmeter, Brooks 5850S), the flowrate had to be measured by deriving the flow to a calibration reservoir every time it was modified. Even so, it was very difficult to precisely measure hysteresis loops. Going from filling to emptying, or reversely, involves the manipulation of valves, and associated errors in the amount of helium in the experimental cell, which accumulate over repeated cycles. This precludes any precise determination of the temperature at which the hysteresis loop disappears.

A solution would be to use the method of Herman *et al.*⁷. These authors directly measure the adsorbed amount in the gel by a capacitive technique. This however requires to plate the porous medium with electrodes. Here, we present a more general alternative, where the adsorbed amount is controlled through the temperature of a helium gas reservoir connected to the experimental cell. For a given amount of helium in the whole system, varying the reservoir temperature transfers atoms from the reservoir to the cell, or reversely. For a given temperature, the amount of adsorbed helium will be the same, independently of the previous history. For large enough pressures, this provides an efficient way to control this amount.

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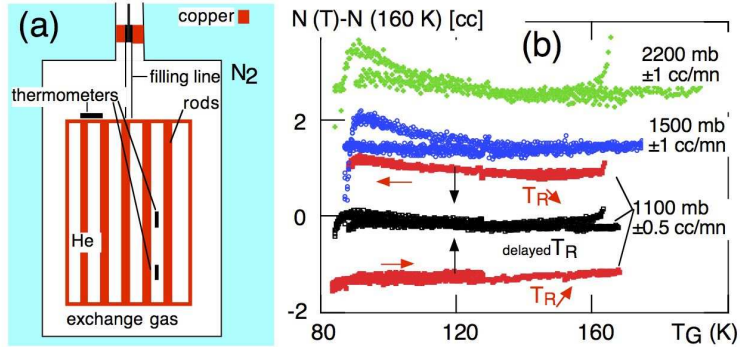


Fig. 1. (a) Sketch of the reservoir. (b) Temperature dependence of the computed total amount N_T of helium (in STP cm^3). The curves correspond to three loading pressures at 160 K. For the 1100 mb data, N_T computed taking the gas temperature T_G equal to the reservoir temperature T_R presents a ± 1 STP cm^3 hysteresis between filling and emptying. This hysteresis is suppressed when assuming a 60 s thermal lag between T_G and T_R . The same lag suppresses the hysteresis for the 1500 and 2200 mb data as well (for clarity, the corresponding curves are vertically shifted).

2. Constraints and design

The design parameters of the system are set by a number of constraints. First, the reservoir volume and the temperature range of operation are fixed by the amount to transfer. Second, the reservoir design should be such that the gas temperature remains homogeneous when the heating power is varied, i.e. the static and dynamic gradients should be as small as possible. Third, the coupling of the reservoir to the cold source should be good enough to allow cooling at the required rate (heating being not a problem).

We use a cylindrical copper reservoir (10 cm long, 6.5 cm diameter, with 2.5 mm thick walls, and approximate volume 230 cm^3), inside a vacuum can immersed in a tank of liquid nitrogen (Fig.1(a)). The 1×1.5 mm filling line has a volume of less than 1 cm^3 . At a constant pressure of P bar, varying the reservoir temperature from 80 K to 180 K results in a transfer of about $400 P$ STP cm^3 . This is more than needed to cover the steep part of the isotherm for $T > 4.2$ K in a 0.5 cm^3 aerogel (Fig.2). There are three paths for the thermal contact to the nitrogen bath : conduction through the 3×4 mm stainless steel tube to which the reservoir is suspended, thermal radiation to the walls of the vacuum can, and conduction through the exchange gas (air). This latter contribution dominates by a factor of order 20 in our conditions, where the exchange gas pressure is of order 50 Pa, at the crossover between

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the molecular and hydrodynamic regimes of heat transfer. This choice allows a good thermal coupling, with a nearly uniform cooling power on the external surface of the reservoir. Heating power is provided by a 60 ohms manganin wire heater wound on the external faces of the reservoir, in such a way that the area enclosed between two turns is approximately constant. We expect this design to ensure an uniform temperature of the copper. In order to maximize the thermal coupling to the gas, the reservoir is also traversed by twenty-four 4 mm diameter copper rods, soldered about 12 mm apart on its top and bottom faces. A platinum resistance, glued on the top face of the reservoir, is used for regulating its temperature, while two platinum resistances inside the reservoir read the gas temperature between two rods (at mid-height and close to the bottom).

The reservoir temperature is regulated with a maximal heating power of 10 W, allowing to go from 80 K up to 160 K in one hour. The minimal time (heater off) to come back to 80 K is of order of four hours. The maximum flow rate which can be obtained over the whole temperature range is 2 cm³/minute for filling and 0.5 cm³/minute for emptying. These values are more than enough for studying aerogels.

3. Accuracy

We first studied the accuracy of the system by coupling it to a temperature regulated reference reservoir at 305 K. For a given total amount of helium, the pressure of the whole system was measured as a function of the cold reservoir temperature, from which we computed the amounts N_C and N_W of helium in the cold reservoir and the remaining of the system (reference reservoir, pressure gauge, and connecting lines at regulated ambient temperature, plus filling line to the reservoir). Experimental volumes were determined at ambient temperature by expanding gas from the reference volume to the other parts of the set-up, and measuring the pressure changes. We calibrated our thermometers from one of our experimental runs, using our cold reservoir as a gas thermometer. This gives the correct boiling nitrogen temperature within 0.1 K. For other runs, $N_C + N_W$ has to be constant over the whole temperature range, independently of the rate of variation of temperature (which is set by the requested flowrate) or of the coupling to the cold source (i.e. of the exchange gas pressure). Results for a loading pressure of 1100 mbar at 160 K are shown in Fig. 1(b) for filling and emptying at ± 0.5 cm³/minute. The clear 2 cm³ hysteresis is much larger than what could be expected from the impedance of the filling line¹⁰, or from the possible changes in its temperature profile. It results from a

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delay between the reservoir temperature T_R and the gas temperature T_G , evidenced by the inner thermometers. Their measured delay time (65 to 75 s) is much larger than computed from the thermal diffusivity of the gas and the inter-rods distance (between 0.2 and 1 s depending on temperature and pressure). This indicates some unexpected thermal resistance within the copper, or between the copper and the gas. Anyway, this delay time can be efficiently corrected for. Using $T_G = T_R - \tau \dot{T}_R$ with a delay time $\tau=60$ s to compute N_C suppresses most of the hysteresis for all temperature, pressure, and flow rates studied, as illustrated by the corrected curves in Fig. 1(b). All together, the precision and reproducibility are better than one STP cm³, on a total of 200 to 350 transferred STP cm³ (depending on pressure), for flow rates up to 2 cm³/minute. Dynamic temperature gradients are thus not a problem. Static gradients are not a problem either : when the exchange gas is pumped at a constant reservoir temperature of 160 K, which results in a decrease of the heating power from 6 W to 0.3 W, the calculated total amount changes by less than 1 STP cm³.

4. Application to aerogels

We used this device to perform adsorption and desorption isotherms at 4.7 K on a neutrally catalyzed aerogel¹¹. Figure 2a shows that the inferred condensed fraction compares well to our former results¹¹. The remarkable point is that the perfect closing of the loop at the lower pressures is now much easier to obtain.

With the new system, the temperature control offers the possibility to easily perform complex paths in the (pressure-adsorbed amount) plane. This is illustrated by Fig 2b. The lines internal to the main hysteresis loop are obtained by reversing from filling to emptying , or reversely, while being on the hysteretic part of the adsorption loop (they are the so-called scanning curves). These operations, which are delicate when using the flowmeter, become trivial here. Also, it is easy to fill or empty in steps of finite size (grey lines), by changing the temperature set point by steps. As we explained in the introduction, this strongly perturbs the system, probably reflecting the change of the saturated vapor pressure due to local heating or cooling. The interesting fact is that, once the change is relaxed, the final state on the desorption branch coincides with that obtained for slow emptying (0.07 STP cm³/minute). There is a difference on the adsorption branch, but future work is needed to know whether this is due to the larger flowrate used for continuous filling (0.2 STP cm³/minute). In any case, the important thing is that the temperature control is well adapted for studying the relaxation

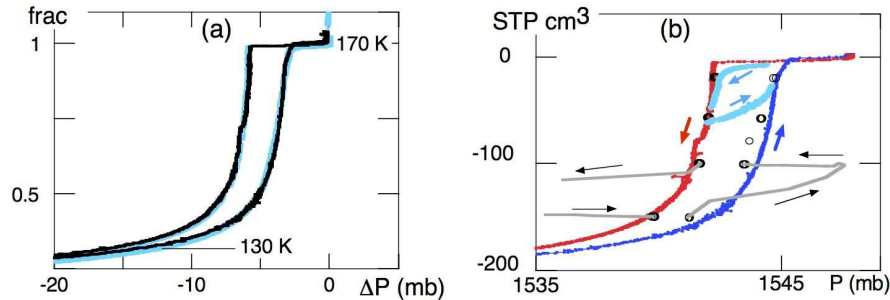


Fig. 2. (a) Adsorption isotherm at 4.7 K for aerogel N102 ¹¹. Condensed fraction as a function of ΔP , the pressure difference with the saturation pressure, for the new (black) and the previous (grey) data. The reservoir temperature is indicated for two points; (b) Comparison of continuous filling/emptying and of finite steps (open dots). The adsorbed amount is referred to the filled aerogel and expressed in STP cm^3 . Some transients are shown (grey lines). Two scanning curves are also shown.

processes in adsorption and desorption.

In conclusion, the set-up we have developed offers an easy and precise control of the adsorbed amount in a porous system. It is thus ideal to study hysteresis, relaxation, and metastable states in the adsorption and desorption of fluids in porous media.

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